dark tachylytic belt formed between it and the clear basalt-glass. × 120.

6. Portion of the same preparation, showing the sharp division of the tachylytic belt from the clear basalt-glass. × 120.

IV. "On the Relation between the Thickness and the Surface-tension of Liquid Films." By A. W. Reinold, M.A., F.R.S., Professor of Physics in the Royal Naval College, Greenwich, and A. W. Rücker, M.A., F.R.S. Received May 15, 1886.

(Abstract.)

Plateau, Lüdtge, and van der Mensbrugghe have investigated experimentally the relation between the thickness and surface-tension of thin films. None of these observers, however, have used films thin enough to show the black of the first order of Newton's colours. The authors have therefore made a careful comparison of the surface-tension of black films with that of coloured films, the thickness of which was from 10 to 100 times greater. The principle of their method is the same as that utilised in Lüdtge's experiments. The interiors of the films to be compared are connected, and the relation between their surface-tensions is deduced from measurements by which their curvature is determined. In the authors' experiments a cylindrical film was thus balanced against another, which, though sometimes cylindrical and sometimes spherical, was initially of the same curvature as itself. The necessity for this arrangement arises from the fact that the authors' previous observations have shown that a film thins to the black of the first order more readily if it is cylindrical than if it is of any other form. The fact that small changes in the forms of cylindrical and spherical films, attached to two circular rings, convert them into unduloids or nodoids, renders the mathematical theory somewhat complicated, but other considerations have been made to give way to the necessity of obtaining films which readily yield the black.

The *sensitiveness* of the methods employed by the authors and by previous experimenters is investigated. All these methods depend upon the measurement of a length, such as the change in the diameter of a cylinder, or in the sagitta of a spherical segment (Lüdtge and van der Mensbrugghe), or the displacement of the liquid in a manometer tube (Plateau).

Let an increment $d\mathrm{T}$ in the surface-tension T produce an alteration $d\mathrm{L}$ in this length. The fraction $\mathrm{T}\,d\mathrm{L}/d\mathrm{T}$ is taken as a measure of the *sensitiveness* of the experiment. If $d\mathrm{L}$ and $d\mathrm{T}$ are infinitely small, this

is called the limiting sensitiveness. In any experiment the observed value of dL divided by the sensitiveness gives the fractional change of surface-tension.

The numbers expressing the sensitiveness indicate the relative merits of the different experimental arrangements. Some of the authors' experiments were more sensitive than those of any previous observer, but the possibility of improvement in this direction is limited by the fact that if the arrangement is too sensitive the films do not remain sufficiently steady for accurate measurement.

The apparatus and method of observation are then described. Preliminary experiments were instituted to test the observations of Lüdtge and van der Mensbrugghe as to the difference of surface-tension between two films one of which had been formed more recently than the other. These experiments showed that when one of the films was kept thick by supplying liquid to its upper support (flooding), while the other was allowed to thin, a considerable apparent difference of surface-tension was obtained. Before, however, this could be accepted as a trustworthy determination of an actual difference of surface-tension, several possible sources of error had to be considered. Thus, experiment shows (1) that the fact that the thicker film displays the greater surface-tension cannot be attributed to any peculiarity of the apparatus or mode of thickening adopted; and (2) that it is not due to the weight of the thicker film.

It was also important to determine whether the gradual disappearance of the liquid rings by which the films were attached to their solid supports could produce changes in the forms of the films which would account wholly or partially for the phenomenon observed. Two films of the same surface-tension attached to two rings of different sizes could not both be cylinders, as the curvature and therefore the pressure exerted on the internal air would be different. A difference in the forms of the films might thus be due, not to the difference of surface-tension but to an inequality in the magnitude of their supports. The solid rings were accurately turned to the same diameter, but it was thought possible that the draining away of the small liquid masses by which the thinning film was attached to the solid rings might produce alterations equivalent to a change in the diameters of the latter. To test this the following method was adopted.

Theory shows that provided the form of the film does not differ much from a cylinder, the ratio dT/T can be readily obtained by means of an expression which does not involve the diameters of the supporting rings. To make use of this expression, it is necessary to measure three diameters of the film. The ratio dT/T can also be calculated from measurements of the *principal ordinate* (*i.e.*, the

maximum or minimum ordinate which lies halfway between the rings), and from the sensitiveness, in the calculation of which the assumption is made that the generating curve of the film passes through the edges of the upper and lower cups.

The result of comparing the values of $d\text{T}/\text{T}$ obtained by the two methods was to show that only a small part of the difference of form of two films could be ascribed to a slipping of the film over the liquid attachments to the solid supports.

The method of measuring three ordinates was applied to a great number of films, and gave results from 0·5 to 1 per cent. lower than those obtained from the sensitiveness. In the case, however, of two films which were both flooded, and presumably in the same state, the two methods gave results, the differences between which were both more irregular and less in amount, averaging not more than 0·2 per cent. It is therefore probable that when the bulging or contraction of a film becomes considerable there is a little slipping, though not more than enough to account for a small part of the total change of form observed.

Phenomena similar to those described are explained by van der Mensbrugghe by the consideration that when the surface of a film is being continually renewed, it is cooled, and its surface-tension is in consequence increased. This explanation is shown to be inadequate. A colourless film being certainly 250 times thicker than a black one, the increase of surface-tension due to cooling would be only 0·0016 per cent., whereas in some of the experiments there is evidence of a difference of 9 per cent.

The cause of the phenomenon cannot at present be assigned with certainty. Perhaps many causes are at work. Experiments designed to test the effects of oxygen and carbonic acid on the result, though not conclusive, indicate that the phenomenon under discussion is affected by the nature of the atmosphere in which the films are formed. Reasons are given for the conclusion that it is merely an instance of the difficulty which many observers have found in preserving a liquid surface pure.

On the assumption that the rapid change in the surface-tension of a newly formed film is not due to its thinning, but to a disturbing cause, attempts were then made to eliminate this cause, or reduce it so as to compare films of very different thicknesses.

Two methods of attacking the problem were carried out. In the first the procedure was as follows:—The diameters of two cylindrical films were measured when they were in the same state, an electric current was then passed up one of them in order to thicken it, and after a sufficient length of time had elapsed for the direct effect due to the disturbance produced by the current to pass off, the diameters were again measured. By this means it was possible to compare two

films, one of which was nearly all black, while the other displayed a little black and the colours of the first and second orders. Both films were then allowed to thin, and assuming (in accordance with previous observations of the authors) that that which was already black remained in a constant state, any change of diameter which took place as the coloured film became black, could be regarded as due to changes in the thinning film.

An objection to which this method is open requires discussion. Most of the films observed were partly black and partly coloured. If any difference of surface-tension existed between the different parts, the films would not be cylinders or simple unduloids, but the black and coloured parts would have different curvatures. Measurements based on the sensitiveness would not therefore be trustworthy, if, owing to this cause, appreciable changes took place in the forms of the films, or in the pressures which they exerted upon the enclosed air. It was therefore necessary to investigate the form of a film consisting of two parts of different surface-tensions, assuming that it does not much differ from a cylinder. As a result of the mathematical investigation, a table was drawn up giving the ratio of the change of pressure due to a change of surface-tension affecting a part of the surface, to that produced by an extension of the change over the whole film.

Next follows a detailed description of a number of experiments in which two cylinders were balanced against each other, and the electric current was made use of to influence their rate of thinning. The theory applied to the results of these experiments gave the percentage change of surface-tension due to change of thickness.

In a second group of experiments a cylinder was balanced against a sphere. As a spherical film thins more slowly than a cylinder, a comparison between a thick film (sphere) and a black or partially black film (cylinder) could be made without having recourse to an electric current, and greater differences of thickness were obtained than in the earlier observations.

The differences of surface-tension measured in these observations were very small. They never exceeded 1·5 per cent., and the black films were sometimes more and sometimes less curved than the thicker films with which they were compared. There was no evidence of any regular change in the surface-tension as the thickness diminished, and the average difference between the tension of the black and coloured films as deduced from fifteen experiments was only 0·13 per cent.

The general result of the inquiry therefore appears to be that *when the black part of a soap film forms in the normal way, spreading slowly over the surface, no evidence of any change in surface-tension dependent on the thickness of the film is furnished by a direct comparison of the tensions of thin and thick films over a range of thickness extending from* 1350 *to* 12 *millionths of a millimetre.*

This conclusion is based upon a method of experiment by which a change of $\frac{1}{2}$ per cent. in the value of the tension must have been detected, had it existed, and upon fifteen independent comparisons of the tensions of black and coloured films.

The whole of the observations were carried out under the conditions which the previous researches of the authors have shown to be necessary to maintain the composition and the temperature of the films unchanged.

The authors next discuss the bearing of their observations upon the question of the magnitude of the so-called "radius of molecular attraction." They point out that if the mere equality in the surface-tensions of thick and thin films is to be considered conclusive, they have accumulated much stronger evidence for the statement that the radius of molecular attraction is less than half the thickness of a black film, *i.e.*, $< 6 \times 10^{-6}$ mm. than Plateau produced for the assertion that 59×10^{-6} mm. is a superior limit to its magnitude. They are, however, unwilling to draw this conclusion from their experiments until an explanation is forthcoming, in harmony with it, of the apparent discontinuity in the thickness of the film which always (except under very special circumstances) occurs at the edge of the black.

They are themselves inclined to look upon the sharp edge of the black as evidence of a change in surface-tension due to the tenuity of the film, and to regard the result of their experiments as fixing a superior limit (0·5 per cent.) to the difference of the tension of the black and coloured parts.

As no explanation of the discontinuity at the edge of the black has (as far as the authors are aware) ever been put forward, they conclude by a suggestion which, though no doubt of a speculative character, may serve to draw attention to a subject which is they believe of considerable interest.

They show that the main facts to be accounted for, viz., the discontinuity, the uniform thickness of the black, the wide variations in the thickness of the part of the coloured film which is in contact with the black, and the equality in the surface-tensions of the black and coloured films, could be explained if it were supposed that the surface-tension has a critical value when the thickness is somewhat greater than 12×10^{-6} mm.

The possibility of the existence of such a critical value has been pointed out by Maxwell.* It would be explained by the assumption frequently made in discussions on the nature of molecular forces, that as the distance between two molecules diminishes, the mutual force between them is alternately attractive and repulsive.

* "Encycl. Brit.," art. "Capillarity."